Hydrogenation of Bulk Si From SiN$_x$:H Films: What Really Ends Up in the Si?

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ABSTRACT

It previously has been difficult to quantify the small concentration of H that is introduced into Si by processes typically used to passivate bulk defects in solar cells. A novel method that combines IR spectroscopy with marker impurities in the Si has been used to determine the concentration and depth of H introduced into Si from an annealed SiN$_x$ film. First-principles calculations of structures, binding energies, and local vibrational modes complement the experimental data.

1. Introduction

Hydrogen is commonly introduced into Si solar cells to reduce the deleterious effects of defects and increase the minority carrier lifetime [1-5]. A promising method to introduce H is from a hydrogen-rich layer of SiN$_x$ that is deposited onto the Si to act as an antireflection (AR) coating [4,5]. A post-deposition anneal is used to diffuse H from the SiN$_x$ layer into the Si in order to hydrogenate defects in the bulk Si. Unfortunately, it has been difficult to detect directly the H that is introduced because of its small concentration. Therefore, the effectiveness of the hydrogenation that results from the postdeposition annealing of SiN$_x$ layers has remained controversial [6,7].

In the present paper, a novel method that combines IR spectroscopy with marker impurities that can trap H in Si is used to determine the concentration and depth of H that is introduced into Si from a SiN$_x$ layer. Pt impurities are used as model traps for H because the Pt-H complexes in Si are thermally stable (up to 650°) and their H vibrational absorption lines have been identified [8]. Furthermore, the intensities of the PtH IR lines have been calibrated so that the concentration of H in the Si sample can be estimated [9].

Systematic calculations of the structures, binding energies and local vibrational modes of various traps for H, including N and C, are being performed. The results for NH complexes are reported here.

2. Experiment

To increase the sensitivity of vibrational spectroscopy for the detection of small concentrations of H-containing defects, IR absorption measurements have been made for samples in a multiple internal reflection (MIR) geometry. Samples with dimensions 15 x 20 mm^2 and a thickness of 1.5 mm were made from p-type (~10 Ω-cm) Si. The ends of the samples were beveled at 45º. The probing light was introduced through one of the beveled ends so as to be multiply reflected many times from the internal surfaces as it passes through the sample (Fig. 1).

Pt impurities, to be used as traps for H, were diffused into the Si samples at a temperature of 1225°C. The resulting Pt concentration is estimated to be ~10^{17} cm^{-3} from solubility data in the literature [10]. SiN$_x$ layers were deposited onto the Si samples either by plasma-enhanced CVD or by hot-wire CVD [11]. The substrate temperature for the depositions was ~300°C and the nitride layer thicknesses were ~80 to 100 nm. Samples were annealed in a tube furnace in an ambient of flowing N$_2$. IR absorption measurements were made with a Bomem DA3 FTIR spectrometer equipped with a KBr beamsplitter and an InSb detector. Samples were cooled for IR measurements to near 4.2K with a Helitran, continuous-flow cryostat.
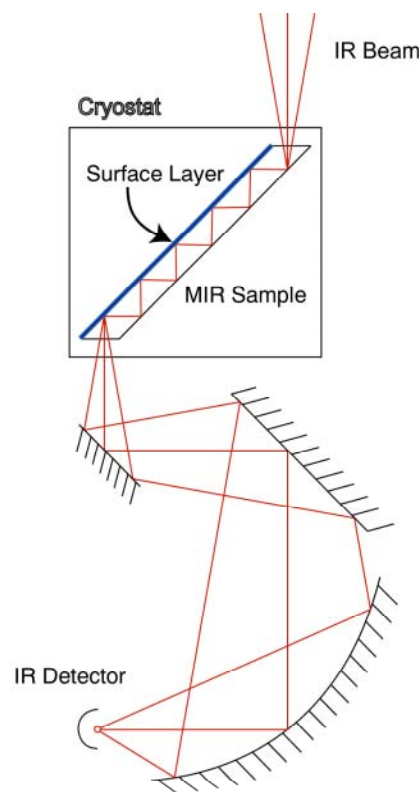
Figure 1. *Multiple-internal-reflection geometry used for IR measurements of Si samples hydrogenated from a SiN$_x$ surface layer.*

3. Experimental Results

IR spectra are shown in Fig. 2 for a Si:Pt sample onto which a SiN_x layer had been deposited. The broad band centered at 2160 cm^{-1} is due to Si-H bonds in the H-rich SiN_x layer. For anneals performed at successively higher temperatures, the Si-H band from the SiN_x decreases in intensity and a H vibrational line at 1880 cm^{-1}, assigned previously to the PtH complex in Si [8], grows in intensity.
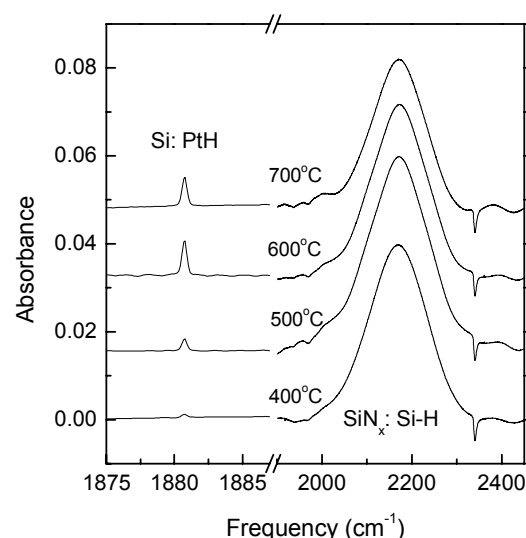

Figure 2. *IR spectra for a bulk Si:Pt sample with a SiN_x layer deposited on its surface by hot-wire CVD. The sample was annealed (10 min.) at the indicated temperatures to introduce H into the Si. Vibrational lines assigned to Si-H bonds in the SiN_x layer and to PtH complexes in the Si are shown.*

Following the anneal at 700ºC, the sample whose spectra are shown in Fig. 2 was analyzed further. The concentration of PtH complexes can be determined from the intensity of the H vibrational line if the thickness of the absorbing layer is known. The sample was mechanically thinned in successive steps in which ~50 to 100 μm were removed from the sample surface onto which the SiN_x had been deposited. The concentration of PtH complexes was determined from the loss of PtH IR intensity as layers of the sample were successively removed. Figure 3 shows the concentration of PtH complexes as a function of depth into the sample. The average concentration of PtH complexes in the first 390 μm of the sample was found to be 4.7 x 10^{13} cm^{-3}. Our previous experience with the trapping of H by Pt impurities in Si shows that it is highly likely that the majority of the H introduced into the Si has been trapped by Pt to form PtH complexes because the concentration of Pt (~10^{17} cm^{-3}) is much greater than the concentration of H [9]. Therefore, the concentration of PtH complexes reflects the total concentration of H introduced into the Si from the SiN_x layer.

The total thickness of the hydrogenated layer can be estimated roughly from these results by assuming that the concentration of PtH complexes is approximately uniform up to a maximum depth after which it falls sharply. The PtH IR signal was reduced by 37% when a 390 μm thick layer had been removed from the sample, leading to an estimate of ~1100 μm for the total thickness of the hydrogenated layer.

IR absorption experiments were also performed for Si:Pt samples onto which SiN_x layers had been deposited by PECVD. Postdeposition annealing also was found to introduce H into the Si bulk to form PtH complexes for these samples.

The results of these experiments show unambiguously that H from a SiN_x surface layer diffuses into the Si substrate during a post-deposition anneal and that this H forms complexes with defects in the bulk. The concentration of H, however, is found to be modest, i.e. near 5×10^{13} cm^{-3} for the experiments performed here. This concentration corresponds to only a few tenths of a percent of the total H that is liberated from the SiN_x coating by the anneal at 700°C. Nonetheless, this is a sufficient concentration of H introduced into the Si to affect impurities like the transition metals that are highly effective lifetime killers.

The modest H concentration introduced by a postdeposition anneal of a SiN_x film is consistent with the sensitivity of the effectiveness of hydrogenation treatments to processing methods [3]. That is, there may be insufficient H to effectively passivate all of the defects that might be present. Therefore, changes in the H concentration that result from differences in processing methods can have a pronounced effect. Experiments are currently underway to investigate the synergistic effect that cofiring the SiN_x AR coating and Al back contact layers has on the improvement of the minority carrier lifetime of solar cells [12,13], and whether this processing synergy might result from the introduction of a greater H concentration into the solar cell.
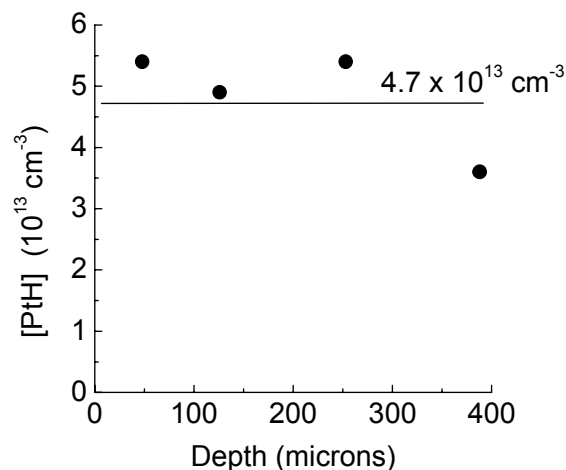

Figure 3. *The concentration of PtH complexes as a function of depth for a Si:Pt sample that was hydrogenated from a SiN_x surface layer during a post-deposition anneal at 700˚C.*

The results presented here also provide information about the diffusivity of H during hydrogenation from SiN_x. An extrapolation of the results measured in 1956 for the diffusivity of H in Si by Van Wieringen and Warmoltz [14] gives a diffusion constant of $D = 3\times10^{-5}$ cm^2/s at 700ºC. For a 10 min. anneal at 700ºC, this value for D gives a diffusion length of 1400 μm. This result is consistent with the thickness of the hydrogenated layer estimated here.

3. Theoretical Work

First-principles theory is now capable of predicting quantitatively structures, binding energies, and local vibrational modes for defects of interest. Typical differences between measured and calculated modes are of the order of 1 to 4% [15]. The purpose of the theoretical research is to examine the *a-priori* possible structures of complexes containing H in order to assist in the identification of any new IR lines that could show up in the experiments. The possible complexes are those involving N (which is abundant in the SiN_x layer), C (very common in EFG material for example) as well as other impurities such as O or selected transition metals.

The calculations are performed using first-principles density-functional theory with atomic-like basis sets using the SIESTA code [16]. The calculations use ab-initio pseudopotentials. The host crystal is represented by periodic supercells (64 to 128 host atoms). These calculations provide geometrical structures, energetics, electronic configurations, and electronic structures. The entire vibrational spectrum is obtained from linear response theory. The eigenvalues of the dynamical matrix are the normal frequencies of the system (including the local modes) and the eigenvectors give the relative atomic displacements associated with each mode.

A theoretical analysis of N-related defects has been performed. We calculated the stable configurations, binding energies, and vibrational spectra of defects which involve a single nitrogen, nitrogen pairs as well as simple NH complexes ($\{N_i,H\}$ and $\{N_s,H\}$). If NH complexes form during the hydrogenation from a nitride layer, these two should be the most abundant and therefore produce the largest IR signals. The complete set of local vibrational modes has been calculated for all these defects and should allow the quick identification of any N-related lines in FTIR spectra. Table 1 shows the calculated frequencies.

Ongoing work deals with carbon-related defects. This includes two $\{C_s,H,H\}$ complexes similar to the well-known H_2^* defect: $\{C_s\!-\!H_{BC}\ldots Si\!-\!H_{AB}\}$ and $\{H_{AB}\!-\!C_s\ldots H_{BC}\!-\!Si\}$ where 'AB' refers to the antibonding site and 'BC' to the bond-centered site. Total energy calculations show that these two complexes are very close in energy. However, their vibrational properties are quite different.

complex	mode	this work (cm⁻¹)	Jones et al (cm⁻¹)	observed
N_i	A'	873	885	
C_{1h}	A'	725	773	
	A"	533	550	
	A"	(293)		
	A"	257		
N_s	E	664	677	653ᵃ
C_{3v}	A_1	(246)		
	A_1	223		
$\{N_i,N_i\}$	A_g	1036	1070	
C_{2h}	B_u	934	968	962.1
	B_u	730	773	765.6
	A_g	705	743	
	A_u	308		
	B_g	(262)		
	A_u	252		
$\{N_i,N_s\}$	A_1	875	1004	
D_{2d}	E	773	774	
	B_2	577	573	
	E	312		
	E	265		
$\{N_s,N_s\}$	E_u	669	669	
D_{3d}	E_g	663	667	
	A_{1g}	320		
	A_{2u}	284		
$\{N_i,I\}$	A	886		
C_1	A	765		
	A	(293)		
	A	255		
$\{N_i,H\}$	A	3229		
C_1	A	1181		
	A	984		
	A	637		
	A	(318)		
	A	(247)		
	A	225		
$\{N_s,H\}$	A_1	1992		
C_{3v}	E	650		
	E	570		
	A_1	316		

Table 1. *Calculated local vibrational modes for isolated N, N pairs, and NH complexes in Si. Only a few of these modes have so far been observed. Jones et al. is Ref. 17.*

4. Conclusion

Vibrational spectroscopy, coupled with the use of Pt marker impurities in Si, has been used to probe the H that is introduced into Si by the post-deposition annealing of an H-rich SiN_x AR coating. The H concentration has been found to be modest in these first experiments, $\sim10^{14}$ cm^{-3}. The thickness of the hydrogenated layer is consistent with the rapid indiffusion of H predicted by the classic results of Van Wieringen and Warmoltz [14] for the diffusivity of H in Si. Systematic calculations of local vibrational modes have been performed to help with the assignment of any new lines following the hydrogenation of the Si samples.

5. Acknowledgments

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